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Separation CF The Pake Platinum Group Elements (Rh, Ir, Ru, Os) by Extraction With Sclvating π-Doncr Ucands and Polymers, in the Thiocyanate

Abraham Warshawsky[a]
[a] Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

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N AND PURIFICATION METHODS, 12(2), 119-141 (1983)

ION OF THE RARE PLATINUM GROUP ELEMENTS (Rh, Ir,Ru, Os) TION WITH SOLVATING π-DONOR LIGANDS AND POLYMERS, IN THE THIOCYANATE SYSTEM.

Abraham Warshawsky [1,2]
Department of Organic Chemistry
eizmann Institute of Science, Rehovot 76100, Israel.

eparation of the secondary PGM (Rh, Ir, Ru, Os) complexes
de media is very difficult due to the existence of the
s in various chemical complexes forms. The formation of
ger thiocyanate complexes allows a much more consistent
n behaviour. The extraction of the PGM thiocyanate
by π-donor solvating ligands and polymers, such as MIBK,
and Amberlite XAD-7 (a methacrylate type polymeric
) was studied. The scheme presented is based on the
n of Ru/Os by selective distillation from thiourea
followed by formation of the thiocyanate complexes of
ual elements. The PGM thiocyanates are passed on XAD-7,
oves Pd, Pt, and then Rh is separated from Ir by
n with [Alamine-336] HSCN. The metals are recovered from
yanate solutions by precipitation as sulfides.

uction

paper is a continuation in line with three previous
ons[3-5] describing modern concepts for the separation of

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platinum group metals (PGM). In the above papers, the principle points in the separation scheme are:

(1) The concentration of the PGM group metal ions and removal from the bulk transition metal elements by selective absorption on isothiouronium anion exchange resin[3].

(2) Elution by thiourea and conversion of the PGM complexes by oxidative hydrolysis back into PGM chloro complexes.

(3) A hydrolytic conditioning step, maintaining Pd,Pt and Au as anionic chloro complexes, and Rh,Ir,Ru,Os (designated as secondary PGM) as mixed aqua-chloro complexes.

(4) Separation of the primary PGM (Pd,Pt) by ion-pair extraction into teriary amine solvent, rejecting the secondary PGM (Rh,Ir,Ru,Os) and base metal ions in the aqueous stream.

(5) Separation of platinum from palladium by selective stripping with sulfur-containing ligands: thiourea for palladium and thiocyanate for platinum.

In continuation of that point the present paper discusses:

(A) Preconcentration of the secondary PGM by various methods.

(B) Test work on several separation schemes, including liquid-liquid extraction, ion exchange and distillation.

2. Concentration Methods

Three alternative concentration techniques were investigated:

(a) absorption on Monivex resin[3],

(b) precipitation as sulfides,

(c) reduction by hydrazine.

The precipitation with sodium sulfide (see Table 1) is fast, quantitative, and allows rapid conversion to the chloro complexes (see Experimental). The absorption on Monivex resin is a more selective concentration method, but requires longer time, and produces a thiourea eluate.

3. Distillation of RuO_4 and OsO_4

Examination of pH-potential equilibrium diagrams[6] for the systems $Ru-RuO_4$ and $Os-OsO_4$ in water at 25°C, shows that in the presence of Cl_2 as an oxidant (E^o=-1.36V), RuO_4 can be distilled at the pH values between 1.5–12, while OsO_4 be distilled at pH values between (-1) and 10.5. The distillation experiments presented in Table 2 show that both RuO_4 and OsO_4 can be distilled from thiourea solutions (i.e. eluate from anion exchange) or from a sulfide precipitate (Table 2c). Selective distillation of OsO_4 (and separation from RuO_4) is achieved when the pH is maintained below 1.5, preferably between 0.1–0.5 M HCl.

4. Extraction of Rh, Ir, Ru and Os from hydrochloric acid by 5% Alamine-336 in solvesso-150.

4.1. <u>From synthetic solutions</u>. Synthetic solutions were prepared by sealed-tube chlorination of the individual metals in the presence of sodium chloride. Under the above conditions, the anionic hexachloro complexes of the secondary PGM are predominant. Under these conditions, Iridium and Osmium are well extracted, in contrast to ruthenium and rhodium, which are poorly extracted (Table 3). Following the extraction from individual metal ion

TABLE I.

Precipitation by Na_2S at pH=10
(metal concentrations in p.p.m.)

	Pt	Pd	Rh	Ir	Ru
Before precip.	50-100	5-50	100-200	10-50	50-200
After precip.	0,08	0,01	0,01	<1,0	0,08

TABLE II

Distillation of RuO_4 and OsO_4

No.	MEDIA	METAL	CONCENTRATION IN SOLUTION (p.p.m.) after time (min)					CONCENTRATION IN COLLECTOR (p.p.m.)
			0	30	120	150	210	
A	1.5% Thiourea pH=3-6	Ru	290		-	40	6	
		Os	980		0	0	0	
B	1.5% Thiourea pH=1.5	Ru	1140	1140				<5
		Os	1000	0				980
C	Sulfide concentrate pH=8→2.5	Ru	240		24	8		

solutions, experiments in extraction from ion mixtures were conducted and are shown in Table 4. In these experiments the ratio of aqueous-to-organic phase volumes were varied in order to determine the maximum loading capacity of the solvent.

In a conclusive counter-current separation experiment, in which an organic solvent consisting of 5% Alamine-336 in solvesso-150 and containing 5000 mg/lit Ir(IV) and 25 mg/lit Ru (III) was contacted with 4M HCl, which scrubbed out efficiently

TABLE III

Equilibrium concentrations and distribution coefficients for the system 5% Alamine -336 in solvesso -150-HCℓ-Rh-Ir-Ru-Os

HCℓ (M)	IRIDIUM			RHODIUM			RUTHENIUM			OSMIUM		
	A (g/ℓ)	O (g/ℓ)	Do/A	A (g/ℓ)	O (g/ℓ)	Do/A	A (g/ℓ)	O (g/ℓ)	Do/A	A (g/ℓ)	O (g/ℓ)	Do/A
0.1	0	0.143	<446	0.119	0.054	0.45	0.042	0.184	4.4	<0.006	>0.196	>65.3
0.2	0	0.143	<446	0.109	0.064	0.59	0.053	0.168	3.2	<0.006	>0.196	>65.3
0.5	0	0.138	<446	0.99	0.074	0.74	0.084	0.120	1.4	<0.006	>0.196	>65.3
1.0	0	0.140	<446	0.118	0.055	0.47	0.104	0.098	0.94	<0.006	>0.196	>65.3
2.0	0	0.138	<446	0.143	0.040	0.28	0.106	0.096	0.90	<0.006	>0.196	>65.3
4.0	0.0003	0.134	<446	0.168	0.005	0.03	0.190	0.042	0.22	<0.006	>0.196	>65.3
6.0	0.010	0.130	13.0	0.168	0.005	0.03	0.205	0.006	0.03	-	-	-
8.0	0.024	0.120	5	0.173	0.00	0	0.230	0.00	0	-	-	-

Strating solution (g/ℓ)· Ir: 0.143; Ru: 0.230; Rh: 0.173; Os: 0.202

A = in aqueous phase; O = in organic phase; A/O = 1:1

TABLE IV

Maximum loading of iridium, ruthenium and rhodium
by 5% Alamine -336 in solvesso -150
from hydrochloric acid (0.1 M).

	IRIDIUM, g/ℓ AT EQUILIBRIUM			RUTHENIUM, g/ℓ AT EQUILIBRIUM			RHODIUM, g/ℓ AT EQUILIBRIUM		
Phase Ratio A/O	A	O$^{(1)}$	Do/A	A	O$^{(1)}$	Do/A	A	O$^{(1)}$	Do/A
2/1	0	0,410		0,54	0,156	2.88	0,110	0,082	0.74
3/1	0	0,590		0,0775	0,156	2.0	0,121	0,090	0.74
4/1	0	0,800		0,086	0,156	1.80	0,125	0,104	0.83
5/1	0	0,980		0,092	0,160	1.72	0.126	0.125	0.99
6/1	0	1,200		0,100	0,160	1.58	0,126	0,150	1.19
8/1	0	2,00		0,134	0,160	1.19	0,134	0,170	1.26
10/1	0	2,00		0,134	0,160	1.19	0,134	0,170	1.26

Strating solution (g/ℓ): Ir. 0,195; Ru. 0,230; Rh. 0,151
(1) Calculated by difference from aqueous phase.
A= Aqueous phase O= Organic phase

the Ru (III), leaving an organic stream of 99.9% pure Ir(IV) (see Experimental).

4.2. *From PGM-Pilot plant solutions.* The extraction results presented in sect. 4.1, were promising enough to attempt a separation of the sec. PGM in real solutions. Those were provided from the aqueous-reject stream from the liquid-liquid extraction pilot plant[4,5]. The history of those solutions included an oxidative hydrolysis (conditioning) step. The results of a counter current extraction experiment on such a solution containing (in mg/lit) Ir -126, Ru -166 and Rh -150 in the same extraction system are presented in Table 5. The results indicate a principal difference in the behaviour of synthetic and pilot plant solutions. The latter incorporate the metal ions in various chemical forms, some extractable, others not. Consequently, the conclusion is that the dilute reject solutions from the primary PGM pilot plant[4,5] cannot be separated by extraction with tertiary amines in the chloride system.

Next, the extraction behaviour of a feed solution obtained by dissolution of a concentrate (see sect. 2) in Cl_2/5M HCl was tried. In Table 6, the metal concentrations, after several consecutive steps of contact with 5% Alamine-336 in solvesso-150 are given, the extraction behaviour of each element is yet again different. Hydrazine concentrates (see Table 6) yield solutions which contain Ir and Ru as two species, with distinctly different extraction behaviour. Sulfide concentrates (see Table 6) yield solutions containing Ir as a non-extractable species, while Ru is mostly extractable. In both cases, Rh is primarily non-extractable.

In conclusion, the extraction studies on synthetic solutions of the secondary PGM in chloride media have revealed that the extraction behaviour is primarily dependent on the sample history, and it is very difficult to maintain a homogenous chemical composition in the chloride media. Logically, this suggests that for that purpose a stronger ligand should be introduced. Sections 6 and 7 describe attempts in that direction.

TABLE V
Countercurrent separation of the aqueous product from pilot plant solution*

METAL	CONCENTRATION AT EQUILIBRIUM, p.p.m.					
	CELL 1		CELL 2		CELL 3	
	Aqu.	Org.	Aqu.	Org.	Aqu.	Org.
Ir	19,0	0	24.0	7,5	30	110,4
Ru	12,0	11,2	22,2	42,5	54,4	192
Rh	145	40	160	40	16,5	21,2

* five times concentrated in 5 M HCl.

A = aqueous compartment; O = organic compartment

A/O = 1:1 Organic phase: 5% alamine-336/solvesso 150

TABLE VI
Extraction from a pilot-plant solution after concentration by hydrazine reduction or sulphide precipitation*

METAL	CONCENTRATION IN AQUEOUS SOLUTION, p.p.m.					
	Before extn	After 1 extn.	After 2 extns	After 3 extns	After 4 extns	After 5 extns
	HYDRAZINE PRECIPITATION					
Ir	970	305	305	305		
Ru	762,5	562,5	572	512,5		
Rh	1 450	1 368	1 337	1 312		
	SULPHIDE PRECIPITATION					
Ir	78,3	78,2	78,2	78,3	77,3	76,8
Ru	383,2	99,2	87,5	82,5	75,0	70,0
Rh	598,3	583,3	566,6	566,6	566,6	568,8
Pt	460,7	19,3	7,3	4,7	0	0
Pd	10,3	1,7	0	0	0	0

* Redissolved in Cl_2/ 5 M HCl.

5. Extraction of Rh, Ir and Ru from perchloric acid solutions.

The distribution of the secondary PGM between solutions of perchloric acid and 5% Alamine-336 in solvesso-150 was determined and is reported in Table 7. The stripping is a non-reversible reaction, as indicated by the large $D_{A/O}$ values for 1-4M $HClO_4$, and the corresponding low $D_{O/A}$ values for the re-extraction reaction. Consequently, perchloric acid can be used for effective stripping of the metal ions from the organic phase, but not as a seperating mediumin counter-current extraction experiments.

6. Liquid-liquid Extraction of Thiocyanate Complexes.

The extraction of thiocyanate complexes of platinum and palladium by Alamine-336 has been reported[4,5]. There, the differences in the rate of formation of the thiocyanate complexes at room temperature were used to effect a separation between Pt and Pd. It was also determined that the formation of the thiocyanate complexes of the secondary PGM required reaction with NaSCN at elevated temperature for 2-5 hours (see Table 8). The extraction of anionic thiocyanate complexes of the PGM by π-donor type extractants are presented in Table 8.

The order of extraction with Alamine-336, tributylphosphate (TBP) and isobutylmethylketone (MIBK) is:

Alamine 336 > TBP > MIBK

Teriary amines are good extractants for the whole group of PGM thiocyanates, except Ir, while phosphoric acid esters (TBP) show a distinction between Ru, Os and Rh and Ir. MIBK shows not only a moderate extraction ability, but also poor phase separation

TABLE VII

Distribution coefficients for the system
$HClO_4$ - 5% Alamine -336 in solvesso -150 (phase ratio 1:1)

$HClO_4$ (M)	IRIDIUM		RUTHENIUM		RHODIUM	
	$D_{A/O}$*	$D_{O/A}$**	$D_{A/O}$*	$D_{O/A}$**	$D_{A/O}$*	$D_{O/A}$**
0,1	0	-	0.3	1.54	0.26	0
0,2	0.016	2.25	0.59	0.11	0.53	0
0,5	0.031	0.87	2.5	0	0.65	0
1,0	15.5	0.83		0	0.88	0
2,0		0		0	0.94	0
4,0		0		0	0.84	0

* Back extraction from organic phase containing (p.p.m.) Ir -155 Ru -140 and Rh -34

** Reextraction from $HClO_4$ solutions containing (p.p.m.) Ir -160 Ru -140 and Rh -16

properties. As we learnt in the chloride system, the single extraction experiments are insufficient, and counter-current extraction experiments are needed to prove that the formation of the thiocyanate complexes is complete, and that their extraction behaviour is consistent with that of a single species.

The counter-current extraction experiments, in the systems 5% Alamine-336 / 2% isodeconal / solvesso-150 against 2M NaSCN, have demonstrated that Rh and Ru can be separated from Ir (Exp. A., Table 9). However, the high acidity of the aqueous solution in that experiment (2M HCl) caused the decomposition of thiocyanate and the deposition of fine sulfur particles which initiated the formation of crud. This was corrected in experiment B (pH=7), and

TABLE VIII

Extraction of thiocyanate complexes

METAL	INITIAL CONCENTRATION (p.p.m.)	CONCENTRATION AT EQUILIBRIUM (p.p.m.)						REACTION COND. FOR THIOCYANATE COMPLEX FORMATION	
		5% Alamine -336		MIBK·HCℓ		50% TBP·HCℓ*			
		A	O	A	O	A	O	Temp (°C)	Time (hr)
Pt	115	0	115	72	43	0	115	94	2
Pd	114	0	114	80	34	0	114	94	2
Rh	170	1	169	169	1	95	75	94	3
Ru	61	0	61	39	22	0	61	94	2
Ir	98	26	78	103	0	68	30	94	2
Os	78	0	78	73	5	0	78	94	5

MIBK = Methyl-isobutyl ketone; 50% TBP = 50%-tributylphosphate in toluene;

A = aqueous phase; O = organic phase.

TABLE IX

Countercurrent separation of the thiocyanates of Rhodium, Ruthenium and Iridium in 2 M HCℓ (experiment A)

METAL	FEED (p.p.m.)	CONCENTRATION (p.p.m.) IN CELL NO:							
		1		2		3		4	
		A	O	A	O	A	O	A	O
Ir	220	153	28.0	163	32.4	20	26.4	18	24.8
Rh	1563	49	420	335	1484	95	1324	54	932
Ru	159	2.5	78.5	25	208	ND	176	ND	161

A = aqueous compartment; O = organic compartment; ND = not detected

consequently, good separation between rhodium and iridium was achieved (Table 10) (see experimental part for the purity of the separated metals).

7. Absorption of PGM-thiocyanates on Polymeric ligands with Oxygen donors.

The liquid-liquid extraction results for the PGM-thiocyanate complexes and π-donor extractants presented in Table 8, suggested that many simple polymeric ligands could be used as separating media for the PGM-thiocyanate complexes. The small extraction coefficients recorded for an oxygen donor, such as MIBK, will be multiplied several times on a chromatographic column. In order to demonstrate this effect, we have selected Amberlite XAD-7, a macroporous, polymeric absorbant. This polyacrylate type polymer, contains $-CO_2R$ type donors, similar to MIBK - has been shown[7] to absorb exclusively $AuCl_4^-$ anions, yet the mechanism of the absorption was not specified. The absorption properties of

TABLE X

Countercurrent separation of rhodium and iridium thiocyanates at pH=7 (experiment B)

METAL	FEED (p.p.m.)	CONCENTRATION (p.p.m.) IN CELL NO: 1		2		3		4		5		6		7		8	
		A	O	A	O	A	O	A	O	A	O	A	O	A	O	A	O
Ir	216	97	ND	97	ND	106	ND	106	ND	106	ND	15	ND	10	ND	75	ND
Rh	368	7.3	25	54	22	56	27	63.5	55	71	315	14	325	7.2	292	5.5	286

A = aqueous compartment; O = organic compartment; ND = not detected

TABLE XI

Absorption of PGM thiocyanate complexes on amberlite XAD-7

	SOLUTION		RESIN	METAL	ELUTION		REGENERATION
METAL	VOLUME (B.V.)	CONC. p.p.m.	VOLUME (ml)	ABSORBED (mg)	ELUENT (2 B.V.)	METAL ELUTED (mg)	ACETONE/HCℓ (mg)
Pd	25	634	20	317	0.2% Thiourea	312	3.2
Pt	5	2140	20	214	H_2O, 80°C	193	
Au	7	192	20	20	0.2% Thiourea	4.0	7.6
Ru	5	140	20	14	0.2% Thiourea	not eluted	
Ir	2.5	200	20	5.6	H_2O, 20°C	5.6	
Rh	2	200	20	6	H_2O, 20°C	6.4	

B.V. = Bed volumes

Amberlite XAD-7 for the individual PGM ions (as thiocyanate complexes) in dilute solutions, were studied and are summarised in Table 11. Obviously, $[Pd(SCN)_4]^{2-}$, $[Pt(SCN)_4]^{2-}$, $[Au(SCN)_4]^-$ and $[Ru(SCN)_6]^{2-}$ are absorbed more strongly than $[Rh(SCN)_6]^{3-}$ and $[Ir(SCN)_6]^{3-}$, indicating that stabilization of higher anionic charges and also steric factors are important factors in determining the absorption coefficients.

Since our main interest in this work is directed to the separation of secondary PGM, a more conclusive experiment in which

TABLE XII

Separation of PGM thiocyanates on XAD-7 column

METAL	SOLUTION CONCN (p.p.m)	MASS (mg)	METAL RECOVERED IN VARIOUS STEPS (mg) OUTFLOW	1 M HCℓ WASH	WATER ELUTION	$C\ell_2/H_2O$ REGENERATION
Pt	11.6	23.2	<D.L.	<D.L.	<D.L.	<D.L.
Pd	1.7	3.4	<D.L.	<D.L.	<D.L.	<D.L.
Ru	29.4	58.8	<D.L.	<D.L.	<D.L.	20
Ir	500	1000	724	78.3	193	41
Rh	500	100	<D.L.	<D.L.	610	317.5

<D.L. = less than detection limit

the initial solution was adjusted to contain mainly Ir(III) and Rh(III) is presented in Table 12. In the absorption step, all of the primary PGM [Pt(II), Pd(II)] as well as Ru(III) and Rh(III) are quantitatively absorbed on the XAD-7 column, whereas 72.4% of the Ir(III) passes through the column. Washing with 1 M HCl retains all the absorbed PGM thiocyanate complexes on the polymer. Deprotonation of the weak $Cl-H...O=\overset{|}{C}-OR$ bond by water elutes the weakly held $[Rh(SCN)_6]^{3-}$ and $[Ir(SCN)_6]^{3-}$ by water. The water eluate contains, therefore, only Ir(III) and Rh(III). Thus, an effective purification of these two elements from the primary PGM (Pd, Pt) and the volatile secondary PGM (Ru, Os) is achieved. Regeneration of the polymer is affected by an oxidative ligand exchange on the polymer, converting the $[M(SCN)_4]^{n-4}$ (n=metal ion charge) to $[MCl_4]^{n-4}$ complexes which are not held up by the resin[7].

8. Conclusions

The separation concepts presented in the introduction to this paper have been tested experimentally and were found valid. This allows an extension of the previously described process for the separation of primary PGM (Pd,Pt) to the separation of secondary PGM (Rh,Ir,Ru,Os). This may be done directly on the thiourea eluate of the Monivex ion exchange resin[3], by controlled distillation and separation of Ru/Os (see Table 12), followed by oxidative-hydrolysis, conversion to the thiocyanate complexes and separation on Amberlite XAD-7 of the residual Pd,Pt from Rh,Ir (Table 12), followed by extraction of $[Rh(SCN)_6]^{3-}$ with [Alamine-336]•HSCN, leaving $[Ir(SCN)_6]^{3-}$ in the aqueous stream (Table 10).

Alternatively, a concentrate can be produced by precipation with Na_2S, and this concentrate can be separated by the same sequence of reactions. From the pure separated thiocyanate complexes of the individual secondary PGM metals, it is possible to obtain (see Experimental section) by precipitation with Na_2S, the pure sulfides. Conventional roasting and calcination will lead to metallic products.

9. Experimental

Precipitation by Sodium Sulphide (Table 1).

The following procedure was found to be effective for all the original solutions resulting from liquid-liquid extraction; whether the original solutions were synthetic or from matte-leach residues.

The pH value of the solutions was adjusted to 2.0 by the addition of sodium hydroxide, and sodium sulphide was then added until the pH value was 10.0. The solution was boiled for three hours, after which the pH value was again adjusted to 2.0 (this produced more precipitate). The solution was then filtered.

The concentration of the metals after precipitation is given in Table 1. The precipitate was dissolved in one of two ways: water was added to the precipitate and chlorine gas passed through the slurry while stirring rapidly, or acid was added and chlorine bubbled through at 80-85°C for one hour. A typical solution resulting from the dissolution of the precipitate in 6 M hydrochloric acid had the following analysis (in p.p.m.)

Pt: 461; Pd: 10.3; Rh: 598; Ir: 78.3; Ru: 338

Precipitation by Hydrazine

Five liters of an aqueous solution from the PGM pilot plant (analysis: Rh: 34.7; Ir: 32; Ru: 39.5 p.p.m.) was treated as follows:

The pH value was adjusted to 7.0 by the addition of sodium hydroxide. 5 ml of hydrazine hydrate were added to the solution at a temperature of 70°. After standing for a few minutes, a black precipitate was formed which settled rapidly and was removed by filtration. The analysis of the filtrate was as follows: Pt: 6.1; Pd: <0.5; Rh: 1.1; Ir: 21

100 ml water was added to the precipitate and chlorine gas was passed through the solution for 15 minutes at 70°C. The analysis of the solution was as follows: Rh: 1450; Ir: 970; Ru: 762 p.p.m.

Distillation of RuO_4 and OsO_4

(A) from thiourea solution, pH 3-6 (Table 2A).

The PGM solution was treated with excess thiourea at 100°C for 30 minutes, the pH value was adjusted to 12.0 by the addition of sodium hydroxide. The solution was boiled for 15 minutes, and the precipitate filtered, slurried in water and dissolved with the aid of chlorine gas. The oxides were collected in 12M HCl.

(B) from pH 1.5 (Table 2B).

In this case, the solution was adjusted to pH 1.5 and OsO_4 was distilled off selectively. The best conditions for separation of the two oxides are distillation of OsO_4 from 0.1-0.5M HCl, containing 1-5% thiourea. Adjustment of the pH to 12 or 13, and distillation of RuO_4.

(C) Distillation of RuO_4 from a sulfide concentrate (Table 2).

The sulfide concentrate (50 g) was dissolved in 1M hydrochloric acid and chlorine was passed through at 80-85°C for 30 minutes. The pH value was adjusted to 8.0 and an Ingold type 405 single-jacket glass electrode, introduced for pH monitoring. After the appearance of a yellowish precipitate, chlorine gas was introduced at 85°C and the pH value slowly dropped to 2.5. The purged gas was passed through a scrubbing solution (conc. HCl). The characteristic deep red colour of Ru (IV) developed in the scrubbing solution within a few minutes. After 120 minutes the pH was adjusted to 8 and chlorine introduced at 80°C for 8 hours. The pH value was 3.5 at the end of the experiment. The precipitate behaves in a reversible manner, dissolves at pH 2.0 and reprecipitates at pH 8.0.

Precipitation of O_sS_2 and RuS_2

The distillates from the experiment described in Table 2 were treated with Na_2S, and the precipitate collected, washed, dried and analyzed. The overall purity of O_sS_2 is 99.88%. The impurities (in p.p.m.) are: Rh: 591, Pd: 633, Ru: 0.5, Pt: 0.41 The overall purity of RuS_2 is 99.85%; the impurities are: Rh: 158, Pt: 767, Pd: 53 p.p.m.

Countercurrent separation of iridium and ruthenium.

Concentrated organic feed was prepared (5 percent Alamine-336 HCl in Solvesso-150) containing Ir: 9,000; Ru: 25 p.p.m. The aqueous stream - 4 M hydrochloric acid. The two phases were contacted in a series of three 60 ml cylindrical separating funnels, with high speed stirring for 10 minutes. The organic feed was introduced in cell no. 1, and withdrawn in cell no. 3. The aqueous stream introduced in cell no. 1, and withdrawn in cell no. 3. The metal concentration at equilibrium is given below (in p.p.m.). (A-1 stands for aqueous phase cell no. 1, 0-1 for organic phase 1, etc).

Cell no.

Metal	A_1	0_1	A_2	0_2	A_3	0_3
Ir	250	8 500	352	8 500	124,5	8 500
Ru	6,6	3,7	15,0	3,0	5,6	0,7

The formation of thiocyanate complexes in chloride solutions at pH 7.0

Solutions (100 p.p.m.) of the chloride complexes of Pt (IV), Pd (II), Rh (III), Ru (IV), Ir(IV), Ir (III) and Os (IV), were adjusted to a pH value of 3.0. Sodium thiocyanate was added so that its concentration was 5 g/lit and the progress of the reactions was followed at 20°C and 94°, by a Hitachi-Perkin-Elmer Coleman 124 double-beam spectrophotometer.

At room temperature, platinum and palladium thiocyanates form rapidly. The rhodium complex form very slowly (the conversion is only 20 percent after 72 hours). Osmium does not form a complex at this temperature, and iridium is difficult to follow since the U.V. bands of $[Ir(SCN)_6]^{3-}$, are masked by the absorption bands of SCN^-. Ruthenium undergoes fast hydrolysis reactions.

At 94°C, platinum, palladium, rhodium and even osmium form complexes fairly rapidly, 5 hours are required for complete formation of the osmium complex. Ruthenium and iridium probably form their complexes fairly quickly, but this is hard to determine.

Absorption of PGM thiocyanates on Amberlite XAD-7 (Table 11).

The PGM thiocyanate complexes are passed through columns containing 20 ml of XAD-7 at a flow rate of 1 ml/min, using atomic absorption analysis to monitor concentration in the effluent. Although no attempt was made to reach maximum loading of the columns, it is obvious that Pd (II), Pt (II), Au (III) and Ru(III) are much more strongly absorbed than Rh (III) and Ir (III) (see also Table 12). In the elution experiments, Ir (III) and Rh (III) are readily eluted with cold water, while Pt (II) is eluted with water at 80°C (or with 0.2% thiourea at 20°C). Pd (II) and Au (III) are eluted with 0.2% thiourea. Ru(III) is best eluted with water after conversion of the thiocyanate complex to the chloride complex by Cl_2.

__Absorption of thiocyanate complexes on XAD-7 (Table 12).__

(A) 500 ml of a solution containing the PGM chloride complexes in the following concentrations (mg/lit): Pt: 12, Pd: 1.7, Rh: 56.6, Ru: 29.4 and Ir: 7.5 p.p.m., was adjusted to pH=2 and boiled for 2 hours with 5g NaSCN. The solution was passed though 150 ml XAD-7 preequilibrated with HCl. The metal concentration in the filtrate was: Pt, Pd, Rh, Ru less then 1 p.p.m.; Ir - 7.1 p.p.m.

(B) In a second experiment, the same solution (2000 ml) was adjusted to the following concentrations: Rh and Ir, 500 p.p.m.; Pt, Pd, Ru, as above. Then treated at pH=2 with 25 g NaSCN at 70°C for 3 hours and then passed through 300 ml of XAD-7 preequilibrated with HCl. Again, all the Pt, Pd, Rh, and Ru was absorbed. The column was then washed with 1 M HCl which released only the entrained iridium salt. Elution with water recovered both Rh and Ir. Finally, treatment with chlorine water, released the rest of Rh and Ru (see Table 12).

__Counter-current separation of iridium, rhodium and ruthenium.__

(A) A solution containing (mg/lit) Ir: 220, Rh: 1563, Ru: 159 and 2M NaSCN was kept at 70°C for 4 hours to adjust the metal forms to the thiocyanate complexes. The feed solution was contacted with

5% Alamine-336 in solvesso-150 in a few stages:

Funnel number 1: 5 ml of 5% Alamine-336 and 2% isodecanol in solvesso-150.

Funnel number 2: 5 ml of feed solution in 0.2 M NaCNS, pH=2.

Funnel number 4: 5ml of 0.2M NaCNS in 2M HCl. The added acid caused thiocyanate decomposition and crude formation. For results see Table 9.

(B) A solution containing (mg/lit) Ir: 216 and Rh: 368 p.p.m. as thiocyanate complexes, previously passed through an XAD-7 column served as feed solution, was run against 5% Alamine-336 in eight stages as follows:

Funnel number 1: 5 ml of 5% Alamine-336 and 2% isodecanol in solvesso-150.

Funnel number 5: 5 ml of feed solution in 10 g NaCNS per litre, pH=7.

Funnel number 8: 5 ml of 0.2 M NaCNS in H_2O.

In this experiment, clear phase separation was observed. For results see Table 10.

Precipitation of IrS_2 and RhS_2

The separated $[Ir(SCN)_6]^{3-}$ and $[Rh(SCN)_6]^{3-}$ described in Table 10, were treated with excess Na_2S. IrS_2 was precipitated directly in the 0.2 M NaSCN solution, while $[Rh(SCN)_6]^{3-}$ was first stripped from the organic phase with 0.1 M NaOH and then precipitated with Na_2S. The spectrographic purities of those products are:

IrS_2: contains (p.p.m.) Pt: 40, Pd: 91, Ru: 82 Rh: 0.44, purity: 99.97%.

RhS_2: contains (p.p.m.) Pt: 72, Pd: 83, Ru: 70 and Ir: 0.13, purity: 99.98%.

References and Notes

1. This work was started while the author was employed by The Council for Mineral Technology (formerly, The National Institute for Metallurgy), Randburg, South Africa, in collaboration with Monica M.B. Fieberg.

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